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Metalloaromaticity

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Abstract

Metalloaromaticity is the manifestation of aromatic properties in the chelate metallacycle, and was first described by Calvin and Wilson in 1945. The subject has received sporadic interest until recently, mainly due to the vagueness of the term, 'aromaticity.' In the past decade, there has been renewed interest in the concept due to advances in synthesis, theory and the recognition of its importance in reaction mechanisms. The concept is useful in that it unifies the reactivity, magnetic, spectroscopic and structural properties of chelates in terms of the Hückel rule. This review stems from my graduate work with Dr A.B.P. Lever, in which I began to holistically understand the properties of α,α′-diimine complexes in the context of metalloaromaticity. Others had thought along similar lines, and it is the goal of this review to present these perspectives.

Keywords: Metalloaromaticity; Aromaticity; Ring current; Pseudo-aromaticity; Metallacycle; Metallole; Metallabenzene; Heterocycle

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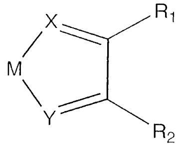
1. Introduction

Although the term 'aromaticity' is not precisely defined so as to allow the unequivocal classification of aromatic compounds [1], it is useful in describing a compound in a brief but encompassing way. The word alone describes the compound's planar, conjugated ring structure; its electron delocalization, ring currents, and tendency toward equivalent, partial bond orders; as well as the manifestations of these properties in NMR chemical shifts, IR stretching frequencies, and $\pi \rightarrow \pi^*$ electronic transitions, etc. It also describes the compound's unusual chemical stability (as compared to other polyenes), its characteristic reactivity in electrophilic substitution reactions, and its ability to stabilize charges on atoms attached to it.

The concept has been applied usefully to heterocyclic organic compounds, but it is only beginning to gain acceptance in connection with chelate metallacycles. A possible reason for this may be that the appearance of aromaticity in chelates has been less predictable than in organic compounds. Hückel's stunningly simple $4n+2$ rule allows one to predict the viability of aromaticity in carbocyclic rings, and if such a simple rule could be applied to chelate metallacycles, one could predict the properties listed above without resorting to complicated quantum calculations. The concept may also be useful in unifying many properties of a chelate that may have appeared disparate. For example, the electronic, vibrational, and NMR spectra, as well as the electrochemistry, and X-ray structure of ruthenium complexes containing quinone-like ligands are easily understood from the viewpoint of aromaticity in the chelate ring [2], as will be described throughout this review. Likewise, the concept of metalloaromaticity should help one to predict and understand various properties of the chelates containing the α,α′-unsaturated fragment, **1**, or the α,β-unsaturated fragment, **2**.



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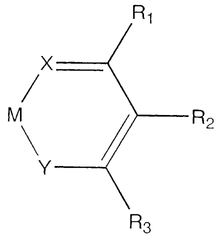

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The concept of metalloaromaticity was introduced by Calvin and Wilson in 1945 to explain the stability of Cu(II)–1,3-diketonate complexes [3], but interest in metalloaromaticity has been sporadic until recently. In the past decade, there has been a growing interest, probably due to advances in synthesis, theory, and the recognition that metalloaromatic intermediates may play an important role in reactions catalyzed by organometallic compounds. The terms 'pseudo-aromatic,' [4] and 'quasi-aromatic' [5] were applied previously in connection with metal chelates, as if to avert controversy. In part, this review is an effort to draw attention to the importance of metalloaromaticity as a useful, molecular-property-unifying concept. Metallocenes have already been discussed in several books and will not be covered here [6].

2. Aromaticity

In organic chemistry, aromaticity is a special state of π-conjugation that occurs in cyclic, planar molecules having $4n+2$ π-electrons (the Hückel rule). Aromaticity gives the molecule unique stability and reactivity. This stability originates from having filled 'shells' of π-orbitals; a shell, being a degenerate set of orbitals. The lowest energy shell of a homocyclic aromatic of D_{nh} symmetry contains one π-orbital; the subsequent shells contain two; and the highest energy shell contains either one π*-orbital for an even-membered ring, or two π*-orbitals for an odd-membered ring. Since the lowest energy shell requires two electrons to fill, and the subsequent shells require four, the Hückel $4n+2$ rule arises (Fig. 1).

The lower symmetry of heterocyclic aromatics causes each two-orbital shell to split into two one-orbital shells of differing energy. The energy splitting increases as the heteroatom's electronegativity deviates from the electronegativity of the other ring atoms, thus, the $4n+2$ rule does not apply rigorously to heterocycles.

3. The isolobal analogy

The basis of metalloaromaticity is evident from Hoffmann's isolobal analogy [7]. An inorganic fragment is said to be isolobal with an organic fragment "if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar — not identical, but similar [7]." The type of reactions that isolobal fragments undergo should be similar as a result; for example, the $Mn(CO)_5$ fragment is isolobal with $CH_3^{\bullet}$ because the singly occupied frontier d-orbital of $Mn(CO)_5$ is very much like the singly occupied p-orbital of the methyl radical. Both fragments dimerize, forming $(CO)_5Mn–Mn(CO)_5$ and $H_3C–CH_3$. Moreover, one fragment can replace the other to give $(CO)_5Mn–CH_3$. By the same token, the substitution of a ring atom in an aromatic molecule with an isolobal metal fragment should preserve the aromaticity in the new molecule.

3.1. α,α′-Unsaturated ligands

As an example, the isolobal analogy can be applied to the benzoquinonediimine (BQDI) complex, **3** [8]. This complex is comparable to the benzimidazolium ion, **4**,

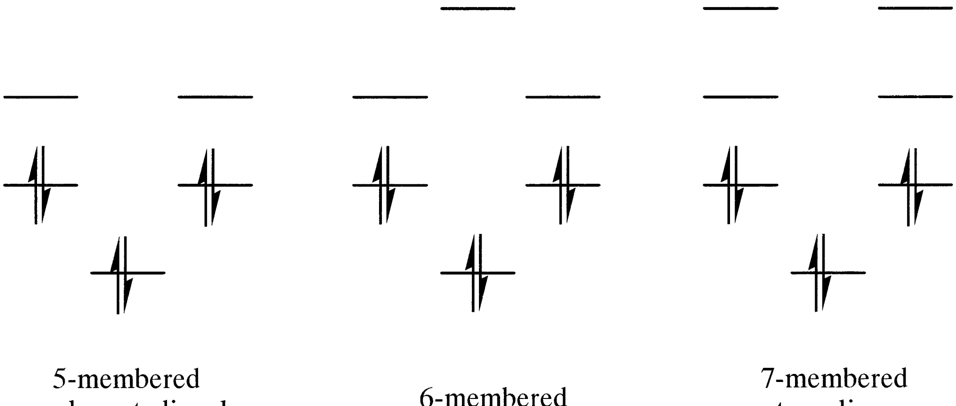
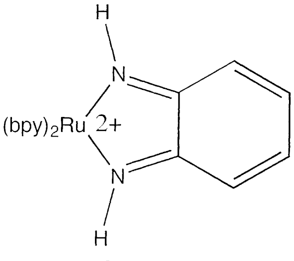


Fig. 1. Examples of the occupation of 'shells' in five-, six-, and seven-membered aromatic rings.

where the $(bpy)_2Ru^{2+}$ fragment is isolobal to the HC^+ fragment. Here, the resonance structure has been drawn in such a way as to emphasize the analogy between organic and inorganic systems [9]. The $(bpy)_2Ru^{2+}$ fragment has frontier orbitals with energies, orientations, occupations and lobe signs similar to those of the HC^+ fragment, albeit one originates from 4d-orbitals while the other originates from 2p-orbitals.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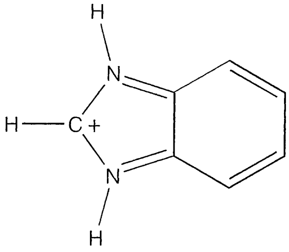
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The isolobal analogy is seen readily using the valence bond approach. The carbon 2s, $2p_x$, and $2p_z$ orbitals combine to give sp^2 hybrids (Fig. 2), which symmetry adapts in C_{2v} to give an $a_1(C)$, a $2a_1(C)$, and a $b_1(C)$ orbital. The $2p_y$ orbital is left unhybridized, and has the symmetry label $b_2(C)$.

The $a_1(C)$ orbital is used to σ-bond with the hydrogen atom, leaving the empty $2a_1(C)$, empty $b_1(C)$, and filled $b_2(C)$ orbitals to interact with the BQDI fragment orbitals. It can be shown that three orbitals of the $(bpy)_2Ru^{2+}$ fragment predominantly interact with the BQDI fragment; an empty $2a_1(Ru)$, an empty $b_1(Ru)$ and a filled $b_2(Ru)$ orbital.

The analogy, as far as the bonding orientations go, is clearly seen in Fig. 3. The $2a_1$ and b_1 orbitals of the HC^+ or $(bpy)_2Ru^{2+}$ fragment σ-bond with, and accept

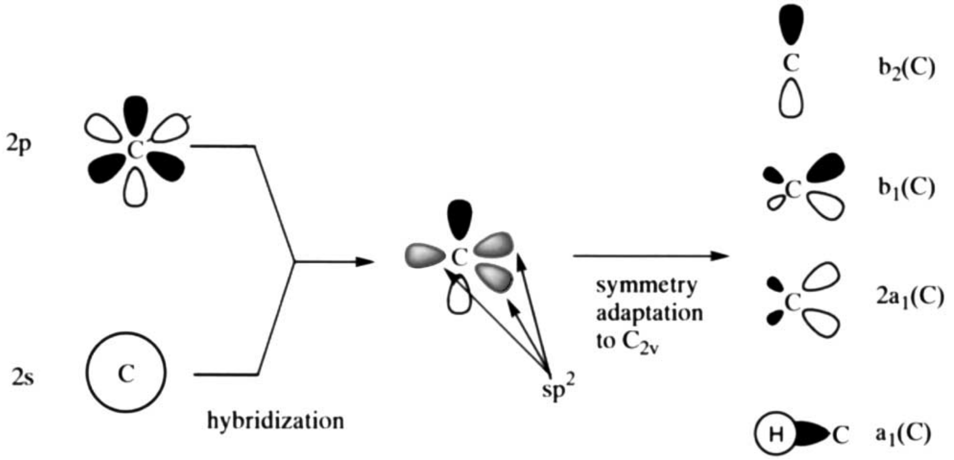


Fig. 2. The hybridization and symmetry adaptation of carbon valence orbitals in the CH^+ fragment.

electrons from, the σa_1(BQDI) and σb_1(BQDI) orbitals of the BQDI fragment. Further, the b_2 orbitals of the HC^+ or $(bpy)_2Ru^{2+}$ fragments π-bond with, and donate electrons to, the π^*b_2(BQDI) orbital.

There is an additional complication with the BQDI system: the five-membered metallacycle can become an aromatic π-sextet by adding two π-electrons from the metal, or the nine-membered periphery of the Ru–BQDI fragment can become an aromatic π-dectet by adding two π-electrons from the metal (Fig. 4).

3.2. *α,β-Unsaturated ligands*

The isolobal analogy can be applied to α,β-unsaturated ligands much in the same way as the α,α′-ligands. For example, 2,4-pentanediiminato chelates can be compared to diprotonated pyrimidine (Fig. 5a and b, respectively). The α,β-unsaturated ligands already have six π-electrons, thus, they must interact with a fragment with an empty p^{π} or d^{π} orbital to maintain the π-sextet. The HC^{3+} fragment fills this need, as it is essentially the HC^+ fragment, discussed in case of the α,α′-ligands, minus the two p^{π}-electrons. The α,β-unsaturated ligands have a highest occupied molecular orbital (HOMO) of πb_2 symmetry and a lowest unoccupied molecular orbital (LUMO) of πa_2 symmetry. Thus, the empty p^{π}-orbital of the HC^{3+} fragment, which has b_2 symmetry, accepts electrons from the πb_2 HOMO of the

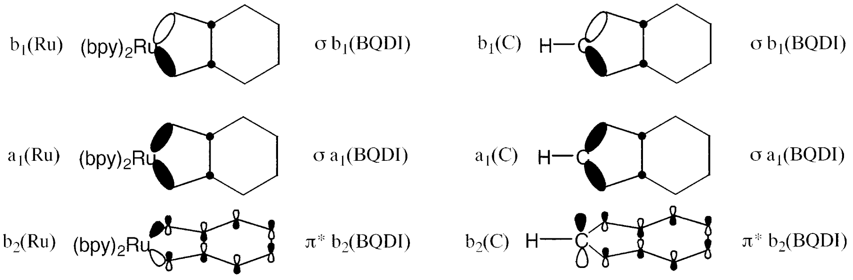
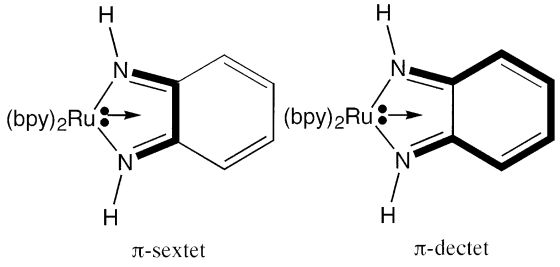


Fig. 3. The isolobal analogy between the $(bpy)_2Ru$ fragment and the CH^+ fragment in the $[(bpy)_2Ru(BQDI)]^{2+}$ complex and in benzimidazolium. The transition metal has orbitals with the correct orientation and sign to σ-bond and to π-bond like carbon.



π-sextet π-dectet

Fig. 4. The Ru–BQDI chelate can be considered to be either an aromatic Hückel π-sextet or a π-dectet.

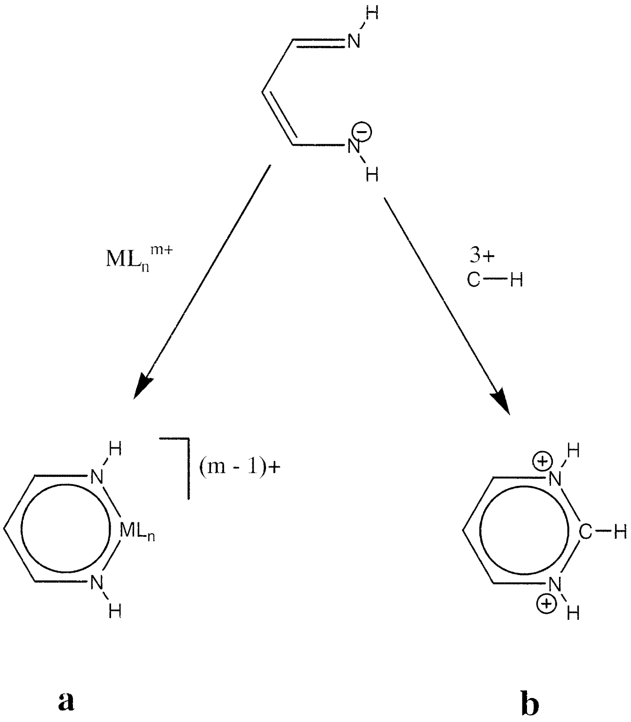


Fig. 5. The diiminato ligand, **a**, can be considered a fragment of the protonated pyrimidine, **b**. The metal fragment ML$_n^{m+}$ must be able to accept two π-electrons from the ligand to be isolobal with the CH^{3+} fragment of the pyrimidine.

α,β-unsaturated ligand fragment. The πa$_2$ LUMO may also play a role in bonding for certain metal fragments, as discussed later.

4. Criteria for aromaticity

Various criteria have been used to judge aromaticity, but no one criterion is satisfactory; instead, it is better to use two or more criteria that are 'orthogonal' to each other [1]; for example, IR frequencies and NMR chemical shifts. Criteria for assessing the relative degree of aromaticity can be divided broadly into three categories: resonance energy stabilization, molecular structure, and magnetic properties.

4.1. Resonance energy stabilization criterion

The resonance energy (RE) stabilization criterion is based on the additional enthalpy that is released by forming an electron-delocalized cyclic structure versus a similar localized reference; i.e. the Kekulé structure. A number of computational schemes that use various reference molecules or fragments have been developed to calculate the resonance energy of organic molecules. In historical order these include the Hückel [10], Dewar [11], Hess–Schaad [12], topological [13], and perturbation MO methods [14]. Simple methods have also been developed to estimate the resonance energies of polycyclic aromatics, such as the conjugated circuit model (CCM) [15] and the structure-resonance theory (SRT) [16].

Quantum mechanical calculations are a more general way of obtaining the resonance energy. Here, hypothetical homodesmotic reactions are conceived in which an aromatic molecule reacts with a reagent to produce acyclic polyenes with the number and types of atoms, bonds, and hybridizations, preserved on each side of the reaction (Eq. (1)). The calculated change in enthalpy of the reaction is then predominantly due to resonance energy. An example is given.

(1)

4.2. Structural criterion

In homocyclic conjugated molecules the degree of bond length alternation decreases from an antiaromatic molecule to an acyclic conjugated molecule to an aromatic molecule [17]. Thus, the equality of bond lengths has been used as an index of aromaticity. One such index, formulated by Julg and Francois [18], is shown below:

$$A = \left[1 - \frac{225}{n}\sum_{r}^{n}\left(\frac{d_r - d_{\mathrm{av}}}{d_{\mathrm{av}}}\right)^2\right]\prod_{r}^{n}\left[1 - \left(\frac{\Delta q_r}{d_r}\right)^2\right] \tag{2}$$

where d_r is the length of the rth bond; d_{av} is the average length of n peripheral bonds in Å; and $\Delta q_r/d_r = (q_i - q_j)/d_r$ is the charge gradient over the rth C–C bond.

Because bond lengths, bond orders and interatomic force constants are related, a group of aromatic indices, the harmonic oscillator model of aromatic stability (HOMAS) indices, have been devised based on each of these parameters. The original formulation of the HOMAS index [19] was based on the sum of the square deviations of bond lengths around the aromatic ring from 'optimal' aromatic values, $d_{\mathrm{opt}}^{a_i a_j}$.

$$\mathrm{HOMAS} = 1 - \frac{98.89}{n}\sum_{r=1}^{n_{a_i a_j}}(d_{\mathrm{opt}}^{a_i a_j} - d_r)^2 \tag{3}$$

$$d_{\mathrm{opt}}^{a_i a_j} = \frac{s + kd}{1 + k} \tag{4}$$

where s and d are, respectively, the bond lengths of a 'pure' single and a 'pure' double bond between adjacent atoms of type a_i and a_j; k is the ratio of the double bond to the single bond force constant; d_r is the experimental bond length; and n is the total number of bonds in the ring. An alternate formulation, HOMAS_p, uses bond orders, P_r, in the calculation [19]:

$$\mathrm{HOMAS}_p = 1 - \frac{3.66}{n}\sum_r^n\left(\frac{2}{3} - P_r\right)^2 \tag{5}$$

In addition, $\mathrm{HOMAS_W}$ and $\mathrm{HOMAS_M}$ are indices based on bond lengths and the quantum mechanically derived Wilberg or Mulliken bond overlap population indices, respectively [20].

The validity of the bond length criterion is supported by the fact that there is a good correlation between the resonance energies calculated from bond length considerations and those calculated from the methods described in Section 4.1. The harmonic oscillator stabilization energy (HOSE) index [21], for example, correlates well with the Hess–Schaad resonance energy:

$$\mathrm{HOSE} = -E_{\mathrm{distort}} = 71.98\left[\sum_{r=1}^{n_1}(R_r^{\mathrm{s}} - R_{\mathrm{o}}^{\mathrm{s}})^2(a + bR_r^{\mathrm{s}}) + \sum_{r=1}^{n_2}(R_r^{\mathrm{d}} - R_{\mathrm{o}}^{\mathrm{d}})^2(a + bR_r^{\mathrm{d}})\right] \tag{6}$$

This index is based on the energy, E_{distort}, required to distort real molecule's bond lengths, R_r^{s} and R_r^{d} (for formally single and double bonds, respectively), into the localized Kekulé structure. Ideal bond lengths, $R_{\mathrm{o}}^{\mathrm{s}}$ and $R_{\mathrm{o}}^{\mathrm{d}}$, and force constants, k_r^{s} and k_r^{d}, for single and double bonds, respectively, are used in conjunction with Hooke's Law to estimate the distortion energy. The force constants are estimated from an empirical equation based on the direct proportionality that is found between k_r and R_r, namely, $k_r = a + bR_r$.

The validity of using bond lengths as a criterion for aromaticity has been questioned [22]. Quantum mechanical calculations have shown that even in aromatic compounds, the π-system is actually stabilized by a distortion toward the Kekulé structure, and it is the σ-system that actually prevents such distortions from taking place [23]. In large annulenes, such alternations in bond length do occur, and the extent of the effect increases as the annulene becomes larger. In benzene, the distortion to the D_{3h} Kekulé structure is favored by the mixing of the $\mathrm{e_{1g}}$ and $\mathrm{e_{2u}}$ π-orbitals, but this mixing is inhibited by the large energy gap between the $^1\mathrm{A_{1g}}$ ground state and the first excited singlet state, $^1\mathrm{B_{2u}}$ [24]. In large annulenes the energy gap between the singlet ground and excited states diminishes, and a second-order Jahn–Teller distortion [25] can cause alternating bond lengths. This energy gap will also decrease if the π-bonding within the ring is weak and, since second row atoms tend to form weaker π-bonds than first row atoms, rings composed of second row atoms, such as hexaphosphabenzene, have a propensity to distort [26].

4.3. Magnetic criterion

It is well known that aromatic molecules exhibit relatively strong diamagnetism when placed in a magnetic field, and this is due to induced ring currents that generate a magnetic field opposing the applied one. This ‘London diamagnetism’ is detected readily in NMR chemical shifts and in diamagnetic susceptibility and diamagnetic anisotropy measurements. On the other hand, antiaromatic molecules exhibit a paramagnetic susceptibility, except for a few that are calculated to be diamagnetic; these are charged molecules having numbers of ring atoms not equal to 4*n* (e.g. $(CH)_3^-$, $(CH)_5^+$, and $(CH)_6^{2+}$) [27]. Thus, aromaticity and antiaromaticity can be distinguished from magnetic properties. The question is whether there is a correlation between the magnetic property and the RE, since one is interested in the *degree* of aromaticity. Such a correlation does exist through Aihara’s equation [28]:

$$\chi = -\mathrm{RE}\left[\frac{eS_N}{\hbar c}\right]^2 \tag{7}$$

where χ is the London diamagnetic susceptibility, S_N is the area of the N-membered ring, and e, $\hbar$ and c denote the usual physical constants. Aromaticity criteria have been proposed based on both NMR [29] and London diamagnetism [30] data.

The main problem in using the magnetic criterion is that the various measurements are influenced by factors other than the RE. For example, ^{1}H-NMR chemical shifts are influenced by inductive effects, and the diamagnetism of localized bonds. Magnetic susceptibility measurements include contributions from the atomic diamagnetism and paramagnetism, not to mention the influence of other aromatic rings in the molecule. Magnetic anisotropies (the difference in diamagnetic susceptibilities parallel and perpendicular to the ring) also include contributions from localized C–C π-bonds and C–H σ-bonds. In benzene, for example, half the anisotropy is due to these effects [31].

A more reliable index of aromaticity is one based on the diamagnetic exaltation; i.e. how much more diamagnetic susceptibility a compound has due to cyclic electron delocalization when compared to a hypothetical structure in which there is no such delocalization. The susceptibility of the hypothetical structure, χ'_{M}, is calculated using an additive scheme, and is subtracted from experimental value for the compound, χ_{M}. The aromaticity index is given by

$$\rho = k\frac{n(\chi_{\mathrm{M}} - \chi'_{\mathrm{M}})}{S^2} \tag{8}$$

where n is the number of π-electrons, S is the area of the ring and k is a scaling factor enabling benzene to be used as an aromatic reference molecule with ρ equal to one.

The ring currents in aromatic molecules generate an induced magnetic field such that there are two roughly conical, magnetically shielded zones extending coaxially from the center of the ring. The NMR of protons in these zones are shifted upfield whereas those outside of the zones are shifted downfield. These shifts have been used to measure the intensity of the induced field, thereby, indicating of the degree of aromaticity. ^{13}C-NMR is not as useful as ^{1}H-NMR in assessing ring currents because the larger diamagnetic and paramagnetic contributions of the carbon atom (it has more electrons) obscure the perturbations caused by the ring currents.

Recently, Shleyer et al., proposed a new criterion of aromaticity based on the theoretically calculated magnetic shielding that occurs at the aromatic or antiaromatic ring center; i.e. the 'nonweighted mean of the heavy atom coordinates' [32]. This criterion, called the nucleus-independent chemical shift (NICS), is based on one of the several magnetically coupled quantum mechanical methods: individual guage for localized molecular orbitals (IGLO) [33], guage invariant atomic orbitals (GIAO) [34], or localized orbitals — local origin (LORG) [35]. The NICS values correlate linearly with the aromatic stabilization energies, with negative values indicating aromaticity and positive values indicating antiaromaticity. The advantage of this approach over the calculation of stabilization energies is that it only relies on the calculation of a single species whereas the latter requires the calculation of several species in a homodesmotic reaction scheme. The disadvantage of NICS, as with all theoretical methods, is that the result depends on the level of the theory, and the availability of basis sets and parameterizations for the atoms involved.

4.4. Stability and reactivity

Resonance energy can significantly stabilize aromatic compounds so that reactions leading to aromatic products are more favorable than similar reactions leading to nonaromatic products. The classic example is the deprotonation of cyclopentadiene ($pK = 16$) to form aromatic cyclopentadienyl anion. The pK of the diene is comparable to that of an alcohol and is many orders of magnitude more acidic than cyclohexene ($pK > 45$) [36]. Conversely, reactions that attempt to destroy the aromaticity of reactants are disfavored over those involving similar nonaromatic reactants. For example, the hydrogenation of benzene to 1,3-cyclohexadiene has an enthalpy of $+5.6$ kcal mol^{-1} whereas the hydrogenation of 1,3-cyclohexadiene to cyclohexene has an enthalpy of -26.5 kcal mol^{-1} [37]. The difference in enthalpy between the aromatic and nonaromatic reference reactions should roughly equal the resonance energy, thereby, providing an estimate of the aromaticity; however, reactions can involve many factors like changes in nuclear configuration, so enthalpy based estimates are not always reliable.

Aromaticity stabilizes intermediates or transition states, thereby, dictating the course of reactions. It is becoming evident that metalloaromatic transition states can play an important role in organometallic reactions. For example, the formation of ruthenabenzene intermediates in the reactions of lithiated butadienyl ruthenium complexes has been studied by Allison and coworkers [38] and Jones and coworkers [39], and tungstenabenzene intermediates have also been implicated in reactions of metallacyclobutadienes with alkynes [40].

Redox reactions, nucleophilic and electrophilic additions, and complexations are all affected by aromaticity, as are valence isomerizations, intra-, and inter-, molecular cyclizations, recyclizations, etc. Compounds that are aromatic tend to restore aromaticity after undergoing a reaction; the so called, regenerative or meneidic ability [41]. Whereas electrophiles add to the double bonds to form a C–C single bond, aromatic compounds retain their bond order by following an electrophilic addition by a subsequent elimination of a weaker electrophile; usually a proton. This occurs due to the thermodynamic stabilization achieved by resonance [42].

5. Evidence of aromaticity in chelate rings

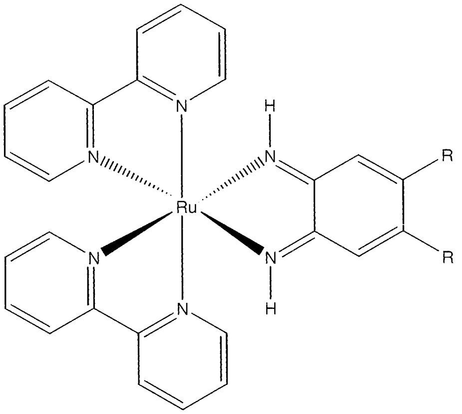
Here, examples are presented in which metalloaromaticity is manifested in various properties including reactivities, electronic structure, molecular structure, and magnetic properties. Metalloaromaticity stabilizes coordinated chelate ligands, allows electrophilic substitution reactions to take place on the ligand, and allows charge-transfer complexes to form with the chelates. The electronic structure and π-electron distribution are also affected as is evident in computational, UV–vis, and XPS studies. Metalloaromaticity affects bond order, and this is apparent in the molecular structure, and IR absorption frequencies of the chelates, and the magnetic properties are affected as can be seen in NMR spectra.

5.1. Reactivity

5.1.1. Stabilization of ligands by coordination

Often in metalloaromatic compounds, an unstable or highly reactive fragment is stabilized by chelation and can become surprisingly inert. It has been suggested that ligands that are the least stable, produce the most stable chelates [43]. For example, the metal-free BQDI ligand is unstable with respect to polymerization and solvolysis and has never been isolated [44], and yet, when the ligand is coordinated, as in complex **5** it becomes exceedingly stable [2]. The complex may be dissolved in concentrated sulfuric acid and in 10% KOH–EtOH solutions with very slow rates of decomposition. It is also inert to fairly strong oxidizing and reducing agents ($E_{1/2}$[oxidn] = 1.37 V; $E_{1/2}$[redn] = −0.45 V vs. SCE). The BQDI ligands are not easily displaced by other ligands and they are not attacked by nucleophiles. It is possible that the stabilization is due to strong π-back bonding [44]. However, only 0.3 electrons are transferred effectively from the metal to the ligand, as indicated by the Ru $3d_{5/2}$ binding energy obtained by XPS [45]. From the viewpoint of metalloaromaticity, a small net charge transfer is sufficient for such stabilization, as will be shown later. Apart from the chelate effect, the conjugated metallacyclic structure of the complex must be involved in the stabilization, after all, complexes of *unconjugated* diimines are unstable with respect to ligand hydrolysis [46].

This stabilization seems remarkable if the ligand is considered to be a detachable, self-contained molecule; however, if the ligand is viewed as a molecular fragment, nothing exceptional has occurred. The BQDI ligand is simply a molecular fragment of benzimidazolium, **4**. This type of stability has also been noted for both α,α′-unsaturated ligands and α,β-unsaturated ligands.

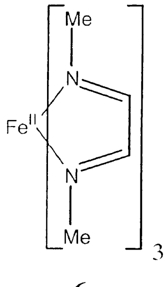


R = NH_2, OMe, Me
H, Cl, NO_2*
*monosubstituted

5

5.1.2. Electrophilic aromatic substitution (EAS)

This type of reaction has been used as an indicator of aromaticity, and is the most widely studied with regards to metalloaromatic chelates [46–49]. Bayer [50] attributed the peculiar reactivity of **6** to metalloaromaticity. The complex is stable in dilute mineral acids and bases, and is not easily oxidized or hydrogenated. It undergoes mercuration, acylation, and halogenation reactions. When treated with bromine in acetic acid, the α,α′-hydrogens of the ligand are substituted for bromine instead of oxidizing the metal as would be expected. Bayer attempted to isolate the Fe(III) oxidation product of **6**, but was unable to do so due to decomposition; however, in situ, it exists long enough to examine it spectroscopically [51]. Two π-electrons must be back donated to the ligand to give an aromatic π-sextet, and a removal of an electron presumably compromises the stability. Bayer noted that **7** is not isolable, and conjectured that this was due to the broken conjugation of the chelate ring. In fact, the literature has few examples [52] of isolable chelates having the general form, **8**, whereas there are numerous stable chelates, containing **1** and **2**.



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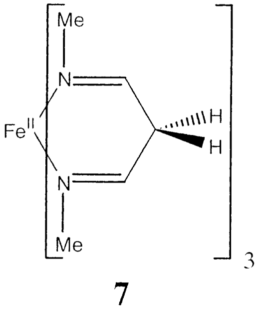

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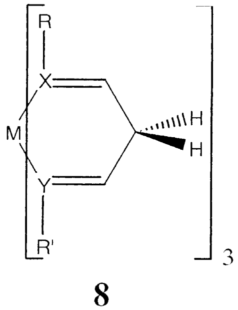

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Collman has studied and reviewed the EAS reactions and physical properties of Cr(III), Co(III), and Rh(III) acetylacetonate complexes [53]. Acetylacetonate complexes are not very stable toward ligand dissociation in acids, thus, EAS reactions were performed using substitutionally inert complexes. The reactions included substitutions of ligand's central hydrogen for I, Br, Cl, SCN, SAr, SCl, NO_2, CH_2Cl, $CH_2N(CH_3)_2$, COR, and CHO. Of the three complexes, Co(III) and Cr(III) are much more reactive toward EAS than Rh(III).

EAS reactions have revealed that there is significant intramolecular, interannular communication in the tris(acetylacetonato) complexes. After EAS occurs on one ring, the subsequent rings progressively become harder to substitute. This is consistent with ^{1}H-NMR studies of the partially substituted tris-chelates, which show that the resonance of the central proton of the unsubstituted ring(s) shifts linearly with the sum of the Hammett parameters of the substituents attached to the complex. These observations raise the unanswered question as to whether the delocalization of π-electrons occur over all three chelate rings.

5.1.3. Charge-transfer complexes

Aromatic molecules form complexes in which an electron donor or acceptor molecule associates with, and partially transfers charge to, the aromatic ring. The formation of such charge-transfer complexes cannot be considered as proof of aromaticity since other nonaromatic π-bonded molecules do the same thing, however, it can be considered as supporting evidence for metalloaromaticity.

Aluminum complexes of 3-nitropentane-2,4-dionate have been shown to form 1:1 charge-transfer complexes with pyridine [54] and quinoline [55], and the square planar dithiolene chelate, $Ni(S_2C_2(CF_3)_2)_2$, forms semiconducting charge-transfer complexes with the polyaromatic hydrocarbons, perylene and pyrene [56]. Interestingly, the one-electron reduced form of this nickel complex also forms a complex with the aromatic, tropyllium cation, $C_7H_7^+$ [57]. Beryllium, Al, Sc, Zr, and Th acetylacetonato chelates [58] and Group 14 4-(ethyl)imino-pentane-2-one chelates [59] form 1:1 charge-transfer complexes with molecular iodine, a reaction first discovered in benzene derivatives [60]. These latter complexes give rise to charge-transfer transitions that correlate linearly with the ionization potentials of the complexes.

5.1.4. η-Bonded complexes

Metalloles are a class of cyclic five-membered ring (C_4R_4E) organometallic compounds that are analogous to cyclopentadiene. Many of these compounds are known to η^5-bond to low oxidation state transition metal fragments such as $M(CO)_3$ and $M(C_5H_5)$. There is theoretical, NMR and X-ray structural evidence that many of the metalloles are indeed aromatic. Various siloles [61], germoles [62], arsoles [63], phospholes [64], ferroles [65], and ruthenoles [66] have equalized ring C–C bond lengths and form η^5-complexes in which M is well centered over the metallole ring. Others such as the iridium [67], rhodium, titanium, hafnium, palladium and cobalt metalloles exhibit some bond localization [68], but still show strong π-backbonding.

The class of six-membered ring (C_5R_5E), organometallic compounds, are called metallabenzenes [69]. Many of these, including phosphabenzene, arsabenzene [70], osmabenzene [71], molybdabenzene [72], and iridabenzene [73], have structures and NMR spectra consistent with aromaticity. The molybdabenzene and iridabenzene complexes also form η^6-metallocenes with the molybdenum tricarbonyl fragment, as does Bleeke's iridathiobenzene complex [74].

5.2. Electronic structure

5.2.1. Computational studies

Quantum mechanical calculations can be performed to understand the origin of the ligand stabilization caused by chelation. The usual method is to calculate the molecular orbital energies of the metal fragment and ligand fragment separately, and then to perform a calculation on the combined complex. The energies of the fragment orbitals that interact in the complex can then be followed to analyze the degree to which they are stabilized in the complex. A similar analysis can be performed on the organic aromatic analog to compare the stabilization of the isolobal fragments. Presumably, if the isolobal fragments are stabilized to the same degree, it is a reasonable argument for the presence of aromaticity.

A comparison of the extended Hückel [75] calculations of the BQDI complex, **3**, and the benzimidazolium ion, **4**, indicates that the stabilization from σ-bonding is poorer in the $(bpy)_2Ru$ fragment than in the CH^+ fragment. This is due to a poorer match in energies between the ligand σ-orbitals and the $2a_1(Ru)$ and $b_1(Ru)$ orbitals as compared to the $2a_1(C)$ and $b_1(C)$ orbitals. The ruthenium orbitals are slightly higher in energy than those of CH^+. The stabilization due to π-back bonding, however, is comparable, being 1.01 eV for the $(bpy)_2Ru$ versus 1.38 eV for the CH^+ fragment. Thus, from the π-system's perspective, the two fragments are isolobal. Similar calculations have been performed on the α,α'-diimine complex, **7**, using a single point SCF-CI calculation [76], and it has been found that the complex is stabilized by 1.39 eV due to extensive π-back bonding. About 30% of the charge-transfer configuration (one-electron excitations from the metal d^π to the ligand π^*-orbitals) contributes to the ground state of the molecule [77].

Calculations allow one to understand how ligand bond lengths are affected by coordination. Back donation of electron density from the metal fragment into a π^*-orbital of the ligand will shorten the ligand bonds over which the π^*-orbital is distributed and will lengthen the bonds where nodes occur. Donation of π-bonding electron density from the ligand to the metal has the opposite effect: the bonds over which the π-orbital is distributed will lengthen, while those having nodes will shorten. This, in fact, is the cause of bond length equalization in the aromatic ring.

5.2.2. Electronic spectroscopy

Chelates that have metal–ligand π-bonds undergo metal-to-ligand (MLCT), or ligand-to-metal (LMCT) charge-transfer transitions. These transitions are depicted in the molecular orbital models, Fig. 6a and b. To determine which of the two molecular orbital models best represents a complex, electron-donor or electron-acceptor substituents on the ligand are varied and the shift of the transition energy is monitored. A bathochromic shift with stronger acceptors indicates a MLCT transition, whereas a hypsochromic shift indicates a LMCT transition. Metal chelates having equally mixed metal and ligand orbitals, Fig. 6c, have a π(metal + ligand)-to-π*(metal + ligand), or MLML, transition whose peak absorption does not monotonically shift with the strength of the donor or acceptor.

The spectra of the BQDI complexes, **5**, have an intense band ($\varepsilon > 10^4$ M^{-1} cm^{-1}) in the visible region that is assigned to a π(Ru + BQDI) → π*(Ru + BQDI) MLML transition. This assignment is confirmed by resonance Raman spectroscopy in that the transition primarily enhances the BQDI modes coupled to Ru–N vibrations, consistent with a transition involving Ru–N bonding and Ru–N antibonding states. The band shifts slightly when varying the BQDI substituents on the ligand, and a plot of the transition energy versus the Hammett substituent $\Sigma\sigma_p$ parameter [78] reveals a peculiar curve (Fig. 7a) that also appears for the π → π* band of substituted benzenes (Fig. 7b). This implies a similarity in electronic structure between the chelate and the aromatic compound. From the metalloaromaticity model, the MLML transition is analogous to the π(HOMO) → π*(LUMO) transition of an organic aromatic compound.

A similar intense band is found in Fe(II), Ru(II), and Os(II) complexes of α,α′-diimines, and Krumholtz [79] attributed the band to "the resonance of π-electrons over the chelate ring." Busch and Bailar [80] observed that this band blue shifts with the number of aromatic rings flanking the chelate ring, (Fig. 8), and tentatively attributed the shifts to the crossed resonance [81] of the metallacycle.

For homologous organic compounds, in which an aromatic ring is systematically perturbed by peripheral structures like substituents and adjoining aromatic rings, the HOMO – LUMO energy gap has been found to correlate with resonance energies and other aromaticity indices [82]. A larger energy gap, and hence a higher transition energy for the lowest energy singlet π → π* band, indicates that the homolog is more aromatic. The existence of this correlation has been rationalized

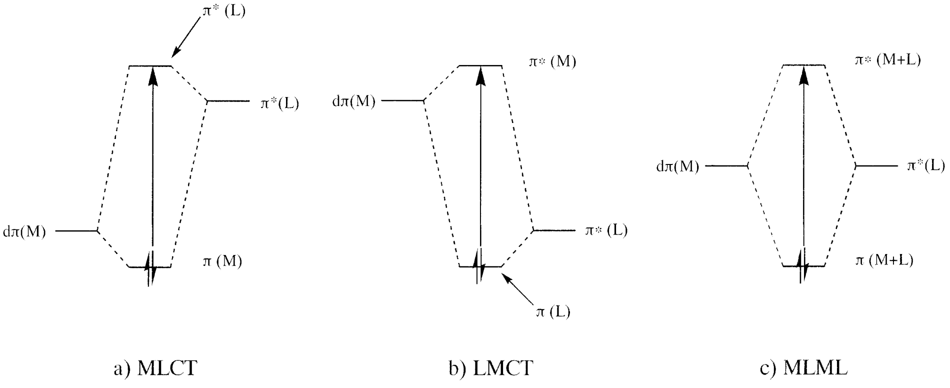


Fig. 6. Three classifications of $d^{\pi} \rightarrow d^{\pi^*}$ transitions: (a) a metal-to-ligand charge transfer (MLCT); (b) a ligand-to-metal charge transfer (LMCT); and (c) a metal-ligand-to-metal-ligand (MLML) transition.

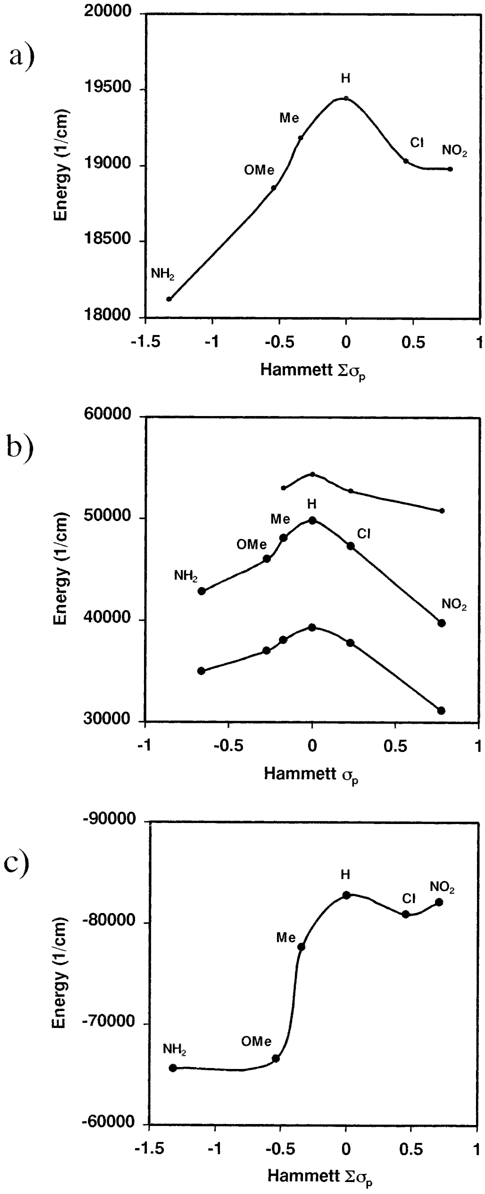


Fig. 7. The effect of various substituents on: (a) the energy of the MLML transition in substituted $[(bpy)_2Ru(BQDI)]^{2+}$ complexes; (b) the energy of the $\pi \rightarrow \pi^*$ transitions in monosubstituted benzene; and (c) the energy of the $\pi(b_2)$ orbital of disubstituted BQDI ligands, obtained using ab initio calculations at the STO3-G level.

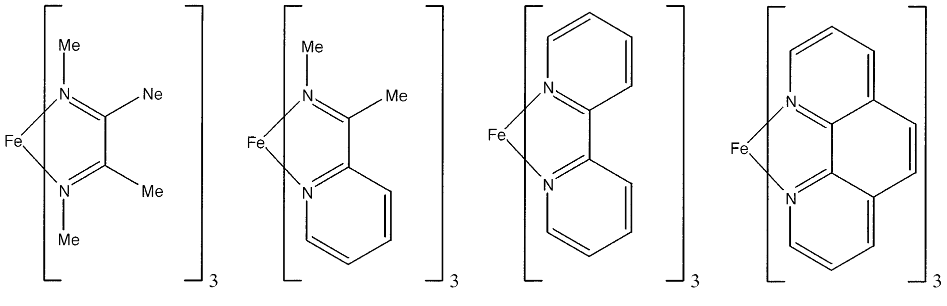
in several ways depending on the aromaticity index in question. For example, the HOSE index is found to be related to the HOMO – LUMO gap through second-order perturbation theory [82].

5.2.3. Photoelectron spectroscopy

X-ray photoelectron spectroscopy can give information regarding the oxidation state of a metal and the nature of the bonded ligands in a coordination complex. The binding energy of core electrons falls into certain ranges for each metal oxidation state, and the variability of the binding energies is predominantly due to differences in the degree of σ-donation of the ligands. The binding energies are lower for ligands that donate more electron density. In metalloaromatic chelates, the ligand π-orbitals become extensively involved in bonding, and these may either donate or accept π-electron density from the metal depending on whether the orbitals are filled or empty. This leads to an ambiguity in the metal and ligand oxidation states.

The Ru($3d_{5/2}$) binding energies [83] of the Ru–BQDI complex, **5**, and $[Ru(bpy)_3]^{2+}$ are 280.9 [84] and 280.5 eV, respectively, as compared to 279.5 eV for $[Ru(en)_3](ZnCl_4)$ and 282.1 eV for $[Ru(NH_3)_6]Cl_3$ [85]. The latter two compounds are reference compounds considered to have unambiguous Ru(II) and Ru(III) oxidation states, respectively. One may also wish to compare $Ru(bpy)_2Cl_2$ (279.9 eV) and $[Ru(bpy)_2Cl_2]Cl$ (281.9 eV) as unambiguous references [86]. The values for metalloaromatic compounds lie in between the values for the Ru(II) and Ru(III) reference compounds; however, some of this intermediacy arises because the σ-donor ability of the BQDI and bpy ligands is worse than the amine ligands. In fact, $[Ru(bpy)_2(1,2\text{-diaminobenzene})]^{2+}$, whose ligand basicity is comparable to the BQDI ligand [87] has a binding energy of 280.4 eV.

From these data, it is estimated that a net charge, equal to about 0.23–0.30 electrons is transferred from the metal to the BQDI ligand. The large stabilization of the ligand by fractional charge transfer can be explained by the metalloaromaticity model. If the six π-electrons of the aromatic metallacycle are equally distributed amongst its five atoms, each atom should have 1.2 π-electrons. Since the ruthenium fragment brings two π-electrons to the metallacycle, it only needs to donate 0.8 electrons to achieve full aromaticity.



(564 nm) > (551 nm) > (523 nm) > (510 nm)

Fig. 8. The effect of flanking rings on the $d^{\pi} \rightarrow d^{\pi^*}$ transitions of Fe(II) (α,α′-diimine)$_3$ complexes. The effect was explained using the aromaticity-based ‘cross-resonance’ concept [57].

5.3. Structure

The intermediate bond orders within an aromatic ring are reflected in the bond lengths and IR stretching frequencies, which lie in the range between those of a single bond and a double bond.

5.3.1. Crystallography

Structural information on metalloaromatic compounds has been acquired almost entirely through single-crystal neutron, and X-ray diffraction, studies. The metal–ligand bond lengths are found to be shorter than a typical single bond, and this is due to the π-donating or π-back bonding interactions between the metal and the ligand. In molecular orbital terms, charge is transferred from the metal or the ligand into an orbital that is bonding with respect to the metal–ligand bond.

The intermediacy in the bond lengths of the chelate must follow as a result of these π-interactions. For the α,α′-ligands, **1**, the π-back-donated electrons go into the π*-LUMO of the ligand, which is antibonding with respect to the X–C and Y–C double bonds, thereby, lengthening the double bonds. Also, the C–C bond shortens because the π*-LUMO is distributed over the C–C bond (Fig. 9a). These effects are evident when comparing the AM1 calculated bond lengths of the free ligand (C–C = 1.513 Å; C=N = 1.291 Å) to those obtained from the X-ray crystal structure of the Ru–BQDI complex, **5** (C–C = 1.434 Å; C=N = 1.303 Å) [88]. It has been shown that metals with different π-back bonding abilities can alter the C–N

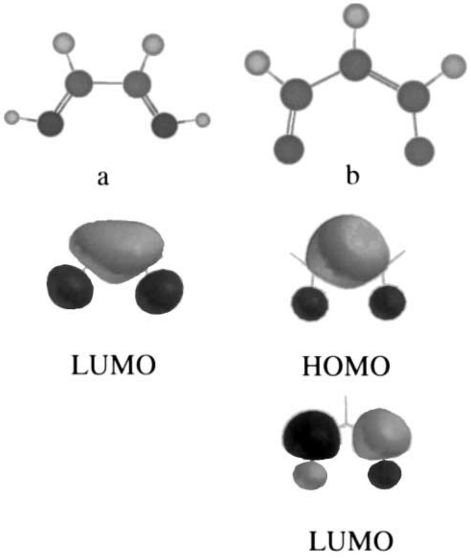


Fig. 9. The frontier π-orbitals of an α,α′-unsaturated ligand (**a**) and of an α,β-unsaturated ligand (**b**). These are the most important orbitals involved in π-bonding with the metal. The HOMO of the α,α′-unsaturated ligand is a σ-type orbital and, therefore, is not shown here.

bond distance continuously from that of a single bond to that of a double bond [89].

For the α,β-unsaturated ligands, **2**, electron density is removed from a π-HOMO that is antibonding with respect to the X–C and Y–C bonds, thereby, shortening these bonds. The π-HOMO is also bonding with respect to the C–C bonds, causing them to lengthen (Fig. 9b). These changes are, in fact, observed when comparing the structures of sodium acetylacetonate (C–O = 1.265 Å; C–C = 1.407 Å) [90] and $V^{III}(acac)_2(THF)_2Cl_2$ (C–O = 1.227; C–C = 1.446) [91]. In contrast, the complexes of form **8** have long metal–ligand bond lengths, short C–X or C–Y bond lengths, and out-of-plane CH_2 groups, indicating very little metal–ligand π-bonding [48c].

5.3.2. Vibrational spectroscopy

The C–N stretch of the BQDI complex, **5**, is assigned to a strong band in the 1330–1420 cm^{-1} region, whose frequency lies between that of alkylaldimines (1675–1665 cm^{-1}) and aromatic amines (1275 cm^{-1}). This reflects a bond order between that of a single bond and a double bond.

Although ab initio calculations of the Mulliken C–N bond orders of the free ligands are insensitive to ring substitution (BO = 1.877 for $R = NO_2$, BO = 1.869 for $R = NH_2$) the experimental C–N vibrational frequency of the complex decreases markedly as stronger electron acceptor substituents are attached to the BQDI ring ($v = 1335$ cm^{-1} for $R = NO_2$, $v = 1413$ cm^{-1} for $R = NH_2$) [2]. This is probably due to an increase in the π-back bonding from the metal, which lowers the C–N bond order.

The BQDI ligand forms a five-membered metallacycle with eight pairs of σ- and π-electrons. In an ideal aromatic ring, these electrons would be equally divided amongst the five bonds, and each bond would have a bond order of 1.60. Alternatively, if the metallacyclic π-dectet is considered (Fig. 4), the bond order would be 1.56. The actual C–N bond order may be estimated from the C–N stretching frequency, using a modification of Hooke's Law [37]

$$\mathrm{BO} = \frac{(2\pi c v)^2 m_1 m_2}{f_0(m_1 + m_2)} \tag{9}$$

where, f_0 is the average force constant for a single bond (5×10^5 dyn cm^{-1}), m_1 and m_2 are the masses of the bonded atoms, and c is the speed of light. The values, thus derived for the substituted BQDI complexes are slightly lower than those obtained from the simple division of electrons between the bonds (BO = 1.35, $R = NO_2$ to BO = 1.52, $R = 2NH_2$)). The discrepancy may be due to the oversimplified bond order estimations, or from deviations from aromaticity. Earlier, Bayer had also attributed the low vibrational frequency of the C–N bond [50] in α,α′-diimine complexes to aromaticity.

5.4. Magnetic properties

5.4.1. NMR spectroscopy

Metallacyclic ring currents, which are usually detected by ^{1}H-NMR spectroscopy, are often cited as evidence of metalloaromaticity. It is important, however, to beware of other deshielding influences such as the inductive or mesomeric effects induced by chelation. A more reliable indicator is the diamagnetic anisotropy surrounding the chelate ring in question. This can be provided by ^{1}H-NMR by looking at the shielding and deshielding of proton probes located above, and around ring's periphery, respectively.

When the spectra of the BQDI complexes are compared to the 1,2-diaminobenzene complexes (these are related by a two-electron–two-proton reduction), substantial differences are observed in the chemical shifts of the bipyridine protons (as much as 0.8 ppm) even though the main structural change is on the *ortho*phenylene ligand. It is unlikely that these differences are due to inductive effects because some bipyridine resonances shift upfield while others shift downfield [2]. The shifts are more consistent with the long-range influence of ring currents associated with the Ru–BQDI metallacycle, whereby the bipyridine protons in the shielding cone of the induced field are shifted upfield while those outside of the shielding cone are shifted downfield (Fig. 10). The BQDI ligand has sp^2-hybridized imine groups that are able

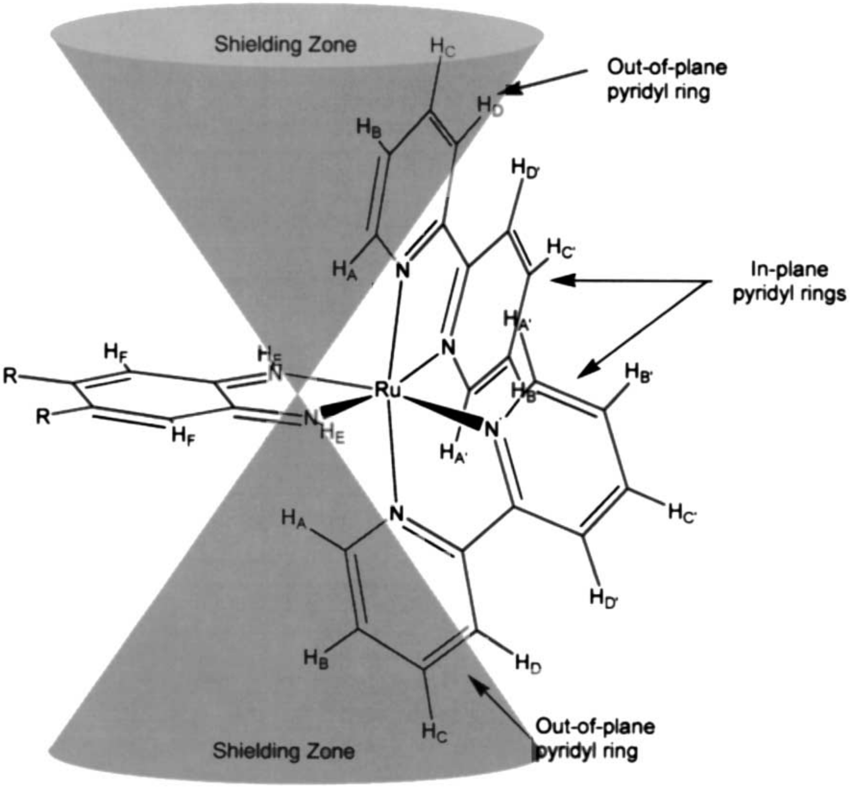


Fig. 10. A picture showing the two types of pyridyl rings in the $[(bpy)_2Ru(BQDI)]^{2+}$ complex. As the Hammett parameters of the BQDI-substituents increase, the NMR of H_A shifts upfield while those of H_E and H_F shift downfield. The NMR of the other protons shifts slightly downfield, except for H_B, which shifts slightly upfield.

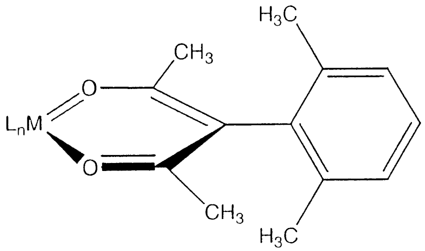
to π-bond with the metal and form an aromatic ring whereas the diaminobenzene ligand has sp^3-hybridized amine groups that are unable to do so. Furthermore, when the BQDI ligand is substituted with increasingly stronger electron withdrawing substituents, a similar effect of opposing shifts in the bipyridine resonances also occurs, albeit less pronounced due to the superposition of inductive effects.

The necessity for π-back bonding is demonstrated most strikingly through the catecholate complex, the oxygen analog of the 1,2-diaminobenzene complex. This complex has unprotonated coordinated oxygen atoms that allow π-interactions, but no low lying π*-orbital to accept the two electrons from the metal fragment; i.e. it already has enough π-electrons to be aromatic. The spectrum for this compound is therefore similar to the 1,2-diaminobenzene complex.

The $[Ru(NH_3)_4BQDI]^{2+}$ complex also displays magnetic anisotropy. The axial amine protons, which are in the shielding cone of the BQDI ring current, are shifted upfield ($\delta = 2.15$ ppm) whereas the equatorial amine protons, which are in the deshielding region, are shifted downfield ($\delta = 4.32$ ppm) [92]. Several groups have attributed the downfield shifts of the CH protons in the NMR of the coordinated α,α′-diimine, to metallacyclic aromaticity [93,94].

There have been numerous claims of aromaticity in the metal chelates of α,β-diketones, based on ^{1}H-NMR chemical shifts. However, these have been disputed by Holm and Cotton [95] because the chemical shift of ligand's central proton varies by only 0.1 ppm for a wide variety of metals whether or not the metals are able to π-bond. Insufficient attention has been paid to the chemical shift contributions from factors other than London diamagnetism. As mentioned earlier, it is important to look at the diamagnetic anisotropy or diamagnetic exaltation. Kuhr et al., have used covalently bound mesityl **9** and anthranyl groups **10** as ^{1}H-NMR probes of the diamagnetic anisotropy around the metallacycle [96]. The anisotropies are small, and there are considerable discrepancies in ordering of the metals using **9** and **10**. In most cases, chelates of alkali metals tend to have lower anisotropies than transition metals including Co(III) and Pd(II), but the only consistent result is that BF_2 and perhaps $B(C_6H_5)_2$ fragments lead to large anisotropies. Using the mesityl probe, Häfelinger et al. showed that there are large anisotropies in transition metal α,α′-diimine complexes [97]. Here, the complex, $Mo(CO)_4$(α,α′-diimine), appears to have greater metallacyclic aromaticity than the Fe^{2+}(α,α′-diimine)$_3$.

Diamagnetic exaltations for transition metal chelates are usually incalculable because the reference parameters for the different types of bonds are not available (see Section 4.3). Several experimental methods have been used, based on comparing the ^{1}H-NMR chemical shifts of the metallacycle in question with that of a similar reference compound in which aromaticity cannot exist. The work of Holm and Cotton [95] is an example of this approach, where the chemical shifts of acetylacetonato complexes that are unable to π-bond with the metal are compared to those that are able to π-bond. Another notable example is that of Daltrozzo and Feldmann [98], in which they compare the chemical shifts of compounds **11**–**13**. The chemical shifts of the H_a proton in **11** and **12** are nearly identical at 4.6 ppm, however, **13**, which is the only aromatic compound, has an H_a chemical shift of 7.1



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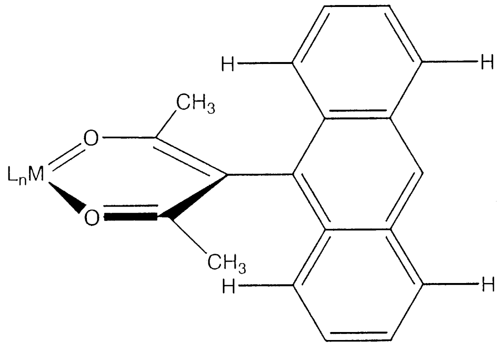

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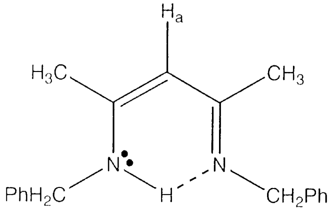
ppm. Strangely, as shall be discussed further, **12** has the stability and reactivity of an aromatic compound.



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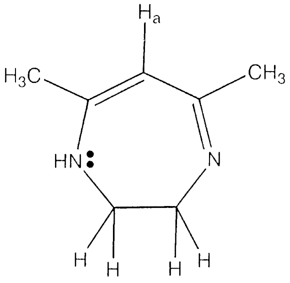

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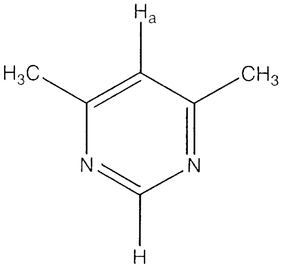

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6. What systems give rise to metalloaromaticity?

Admittedly, without a quantum mechanical calculation, it is difficult to predict whether an arbitrary cyclic molecular structure will be aromatic. The equalization of bond lengths or bond orders depends on the balance between the energetic cost or gain incurred by both the σ- and π-systems when reorganizing localized bonds into delocalized ones, and this in turn, depends on the nature of the ring atoms [1]. This atom dependence is exemplified by the instability of N_6 [99] and Si_6H_6 [100], which are isoelectronic with benzene. However, if a chelate ligand also doubles as a molecular fragment of an aromatic organic molecule, then surely metalloaromaticity can exist in the chelate by the correct choice of metal fragment. There are several factors that are required for this to happen. As mentioned in Section 3, the metal fragment must have the appropriate frontier orbital energies, orientations, and electron occupations, as well as good orbital overlap with the chelate ligand.

6.1. Metal–ligand orbital energy matching

Ab initio calculations [101] and synthesis [102] of the isoelectronic heteroatom analogs of benzene ($X_3Y_3R_6$), have shown that larger differences in the electronegativities of the atoms comprising the ring lead to less aromaticity. However, this is not the only consideration as is evident from Schleyer's calculations of five-membered C_4H_4X systems [33d]. Pyrrole is more aromatic than its phosphine analog and yet the latter has an electronegativity that is closer to that of carbon. Clearly, the frontier orbital energies of the heteroatom must match those of the chelate ligand fragment if 'shells' of π-orbitals are to form as described in Section 2.

The type of ligand donor atoms and the type of metal fragment are of primary importance in matching frontier orbital energies [103]. Stable complexes are formed from soft metal–soft ligand combinations or hard metal–hard ligand combinations. In general, the d^6 metals of the iron family appear to be ideally matched with α,α′-diimine-type ligands. In addition, d^8 cobalt(I) fragments like $(\eta^5\text{-}C_5H_5)Co$ also appear to be well matched with both the α,α′-diimine and tetraazadiene-type ligands [44d]. The planar, d^8 nickel(0) complex, $Ni(BQDI)_2$, also appears to be metalloaromatic [104]. Note that as the nuclear charge of the metal increases, the formal charge on the metal must decrease to compensate for the increased affinity that the nucleus has for electrons. It is also revealing that the ethylenediamine ligands in $[Co(en)_3]^{3+}$ have no propensity to oxidize to the α,α′-diimine form even though they readily do so in the isoelectronic complex, $[Fe(en)_3]^{2+}$. The product in the latter case is the metalloaromatic $[Fe(\alpha,\alpha'\text{-diimine})_3]^{2+}$ complex. The difference probably arises because Co^{3+}, which has a much higher oxidation potential and lower valence orbital energy than Fe^{2+}, cannot donate a pair of electrons to the metallacycle to form a π-sextet as readily as Fe^{2+}.

6.2. Lobe symmetry and orientations

Unlike a carbon fragment, which only has one p^π-orbital that will interact in a π-type fashion within an aromatic ring, transition metal fragments can have two types of d^π-orbital interactions depending upon the structure of the fragment: the a_2-type and the b_2-type (Fig. 11). The b_2-type bonding orientation is analogous to

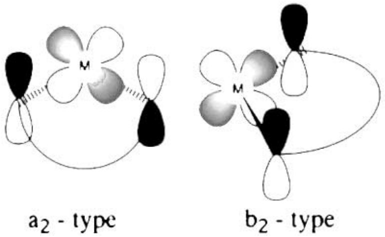

Fig. 11. The two types of π-bonding interactions available to a transition metal chelate: the a_2-type and b_2-type. The latter is the only type of interaction available to a carbon fragment such as CH^+.

that adopted by a carbon p^{π}-orbital, and the Hückel rule will apply if it is the only bonding type that can occur in the metallacycle. Thus, the sum of the π-electrons contributed by the ligand and the metal must equal $4n+2$.

The presence of an a_2-type interaction precludes the use of the Hückel rule. Cyclic structures that are antiaromatic in organic molecules can actually be aromatic in metallacycles [105]. For example, cyclobutadiene is antiaromatic, but $(C_3H_3)W(C–t\text{-}Bu)(MeC{\equiv}CMe)Cl_3$ is metalloaromatic [106]. This type of bonding becomes important in α,β-unsaturated ligands when the b_2 HOMO is unable to donate electrons to the metal fragment due to the complete occupation of the 't_{2g}' set. Thus, fragments like $(bpy)_2Ru^{II}$, which have a d^6 electronic configuration, can only form an aromatic metallacycle through the a_2 π-back bonding interaction with such ligands.

6.3. Electron occupations

In octahedral, tetragonally disorted octahedral, and square planar, low-spin transition metal complexes, the only metal d-orbitals that can π-bond with the ligand are the a_2 and b_2 orbitals. Here, the symmetry labels are loosely used to refer to the two bonding modes shown in Fig. 11. For the α,α′-unsaturated ligand, the b_2 π*-LUMO must accept a pair of electrons from the b_2 metal orbitals, and this means that the metal must have a d^2 to d^{10} electronic configuration. On the other hand, the α,β-unsaturated ligand can either donate a pair of electrons from its b_2 π-HOMO or accept a pair of electrons into its a_2 π*-LUMO. To accept the π-electrons, an octahedrally coordinated metal must have a d^0 to d^4 electronic configuration, and for a tetragonally disorted octahedral or square planar complex, the metal must have a d^0 to d^2 electronic configuration. To donate d-electrons, the metal must have a d^2 to d^{10} electronic configuration. Consequently, only d^2 complexes in general, and d^2 to d^4 octahedral complexes can simultaneously bond utilizing both a_2 and b_2 bonding modes. Of course, to do this, the metal and ligand orbital energies must match.

Since metalloaromatic compounds have metal and ligand oxidation states that are ambiguous, a complex such as the Ru–BQDI complex, **5**, may either be regarded as a Ru(II) fragment interacting with a BQDI ligand, or a Ru(III) fragment interacting with a semiquinonediimine ligand. Once the two fragments are joined and electrons are shared, these distinctions are meaningless, just as it is meaningless to say that carbon monoxide is composed of a C^{2+} fragment and a O^{2-} fragment. In the case of metal dithiolene complexes, the ligand is regarded usually as a two-electron-reduced α,α′-unsaturated ligand, $[SRC{=}CRS]^{2-}$ (R = C_6H_5, CF_3, or CN), bonded to the oxidized form of the metal (Ni(II), for example) [107]. The α,α′-diimine ligand, on the other hand, has never been regarded as a diamidoethylene ligand $[HNRC{=}CRNH]^{2-}$ bonded to the oxidized form of the metal.

These oxidation state ambiguities have more serious implications as is illustrated in the iridabenzene complex mentioned earlier [73]. The unsaturated ligand is effectively the thrice deprotonated form of 2,4-dimethyl-1,4-pentadiene, where two terminal alkene protons and a central methylene proton have been removed. This tri-anionic ligand is the carbon analog of acetylacetonate, and has a similar electronic structure. To form an aromatic metallacycle, it must donate two electrons from its b_2 π-HOMO into a vacant d^{π}-orbital of a metal fragment; in this case, a square pyramidal iridium(III)tris(triethylphosphine) fragment. However, the d^6 iridium(III) fragment has no vacant d^{π}-orbital, and this obstacle is conceptually, if not actually, bypassed by first transferring two electrons from the b_2 π-HOMO into the vacant d_{z^2} orbital of the metal, thereby making a d^8 Ir(I) center and a b_2 π-LUMO on the ligand [69]. An aromatic metallocycle is then achieved by backdonating two electrons from the occupied d^{π}-orbital into the b_2 π-LUMO. Note that this type of electron-transfer gymnastics is only possible because of the appropriate energy levels of the orbitals involved.

7. Survey of metalloaromatic chelates

A survey of the literature in which transition metal chelates are said to have aromatic qualities or appear to have a high degree of delocalization around the chelate ring is summarized in Tables 1 and 2. Chelates with fused aromatic rings such as the 2,2′-bipyridine complexes and macrocycles are beyond the scope of this survey.

Table 1
Examples of metalloaromatic chelates based on α,α′-ligands, $\overline{EXR_1CR_2CR_3Y}R_4$

X	Y	E	R_1	R_2	R_3	R_4	Ref.
C	C	Si	Phenyl	Phenyl	Phenyl	Phenyl	[61]
C	C	Ge	Phenyl	Phenyl	Phenyl	Phenyl	[62]
C	C	$Fe(CO)_3$	Phenyl	Phenyl	Phenyl	Phenyl	[65]
C	C	$Ru(CO)_3$	C_2SiMe_3	C_2SiMe_3	C_2SiMe_3	C_2SiMe_3	[66]
S	S	W	–	p-C_6H_5X	p-C_6H_5Y	–	[128]
S	S	Ni	–	Var.	Var.	–	[128b]
S	S	Ni, Pd, Pt	–	C_6H_5X, alkyl	C_6H_5X, alkyl	–	[128c]
S	S	V, Re, Mo	–	H	H	–	[108,128d]
S	S	Var. metals	–	Var.	Var.	–	[107,109]
C	S	$Ir(PEt_3)_3H$	Me	H	–	H	[110]
N	N	Fe	H	H	H	H	[77,50,80]
N	N	Ru	H	H	H	H	[111]
N	N	Fe, Co	H	Mesityl	H	H	[97]
N	N	Fe, Co, Ni	Me	Me	Me	Me	[112]
N	N	$Mo(CO)_x$–$(P\phi_3)_y$	Var.	H, Me	Var.	H, Me	[113]
N	O	$Mo(CO)_x$–$(P\phi_3)_y$	Var.	H, Me	Var.	H, Me	[114]

Table 2
Examples of metalloaromatic chelates based on α,β-unsaturated ligands, $\bar{\mathrm{E}}\overline{\mathrm{XR_1CR_2CR_3CR_4Y}}\mathrm{R_5}$

X	Y	E	R_1	R_2	R_3	R_4	R_5	Ref.
C	C	$Os(CO)(P\phi_3)_2$	SR	H	H	H	H	[71]
C	C	$Mo(CO)_2$-η^5-pentadienyl	H	Me	H	Me	H	[72]
C	C	$Ir(PEt_3)_3$	H	Me	H	Me	H	[73]
C	O	$Ir(PEt_3)_3$	H	Me	H	Me	H	[115]
C	S	$Ir(PEt_3)_3$	H	Me	H	Me	H	[74]
N	N	Pt, Au	H	Me	H	Me, CF_3	H	[48b]
N	N	Ni	Alkyl	H	H	H	Alkyl	[116]
N	N	Co	Alkyl	Me	H	Me	Alkyl	[47]
N	O	Si, Ge, Sn, Pb	H	Me	H	Me	H	[59]
N	O	Ni, Cu	Alkyl	Me, Ph	H, Cl, Br	Me	–	[117]
O	O	Be, Al, Sc, Zr, Th	H	Me	H	Me	H	[58]
O	O	Var. transition metals	H	Me	H	Me	H	[53,95] and references therein
O	O	Cr, Co, Fe, Ni, Cu	–	Me	H	Furoyl	–	[118]
O	O	Ru	–	Me, Ph	Ru–acac	Me, Ph	–	[122]
S	S	Co, Ni, Pt, Pd	–	Me	H	Me	–	[119]

7.1. Complexes of α,α′-ligands

Some examples of metalloaromatic chelates based on α,α′-ligands are shown in Table 1.

7.2. Chelates of α,β-unsaturated ligands

Some examples of metalloaromatic chelates based on α,β-unsaturated ligands are shown in Table 2.

7.3. Other classes

1. $\overline{\mathrm{MNHCRNHC(NH_2)N}}\mathrm{H}$; M = Cu, Ni, Co, Cr; R = NH–alkyl, O–alkyl; [120]
2. $\overline{\mathrm{MRMRM}}\mathrm{R}$; M = Ge, Ga; R = aryl; [132,133]
3. $\overline{\mathrm{MCHCHC}}\mathrm{H}$; M = W; [105]
4. $\overline{\mathrm{MCRCHCRMC}}\mathrm{R}$ M = Nb; R = $\mathrm{Si(Me)_3}$. [121]

8. Predictive implications of metalloaromaticity

8.1. Electronic analogies

There have been many studies regarding the degree of communication between the metal centers of multinuclear complexes. Greater levels of communication between the metals have been sought as prerequisites to molecular wires or molecular devices, which allow electronic communication over large molecular distances [122]. A better understanding of the factors allowing this communication gives insight into biological electron transfer processes and can be applied to solving technological problems such as the harvesting of light energy. If metalloaromatic complexes parallel the behavior of their organic relatives, one can simply look to the latter for ideas on how to design inorganic complexes so that they communicate. For example, in the binuclear complex, $\mathrm{(bpy)_2Ru(acac\text{-}acac)Ru(bpy)_2}$ [123] (acac-acac = tetra-acetyl(ethanato)), one should be able to easily predict whether the two metal centers communicate by comparing the communication between the terminal carbon atoms of biphenyl. If the communication in the organic relative is small, then it clearly will not be great in the inorganic molecules either.

From the metalloaromatic point of view, it is not surprising that the tetrathiooxalate-bridged, linear polymers of $\mathrm{Cu^{2+}}$, $\mathrm{Ni^{2+}}$, $\mathrm{Pd^{2+}}$, $\mathrm{Pt^{2+}}$, and $\mathrm{Co^{2+}}$ are highly electrically conductive [124]. Each metal atom in the polymer donates two electrons to each tetrathiooxalate ligand to form a π-dectet.

8.2. Structural analogies

The substitution of a carbon fragment in an organic molecule by an isolobal metal fragment should allow the organic molecule to roughly retain its structural properties. The size of the metal atom and the ligands that comprise the fragment may impose steric effects on the molecule of course. For example, if a CH^+ fragment of benzene is replaced by a well-matched metal fragment, the intermediate C–C bond lengths of the benzene should be maintained. It should not be surprising then, that the structure of the tetraiminodiketocyclohexane complex (Fig. 12a) [125] should have a central ring fragment that is identical to anthraquinone (Fig. 12b) [126], and that the two N–Ru–N containing heterocycles of the complex appear to be aromatic as in the (*p*-benzoquinono)-diimidazolium ion (Fig. 12c) [127]. In fact, these analogies should help to predict the structures of inorganic chelates by a simple comparison to their organic relatives.

9. Interannular delocalization

A long standing question regarding metal complexes having more than one chelate ring has been whether the π-electrons are delocalized between two or more rings. This question, which was first raised by Schrauzer et al. for trigonal prismatic metal dithiolate complexes [128], has been revisited for tungten dithiolates [129]. In these investigations one studies how the substituents of a chelate ligand affect another chelate ligand on the complex; for example, by monitoring the NMR chemical shift of the unsubstituted ligand. These interannular effects are often found to be much greater than those expected for 'through-space' or 'through-bond' interactions. As mentioned earlier, Collman has studied this interannular communication through EAS reactivity as well as NMR spectral shifts for transition metal acetylacetonate complexes [53].

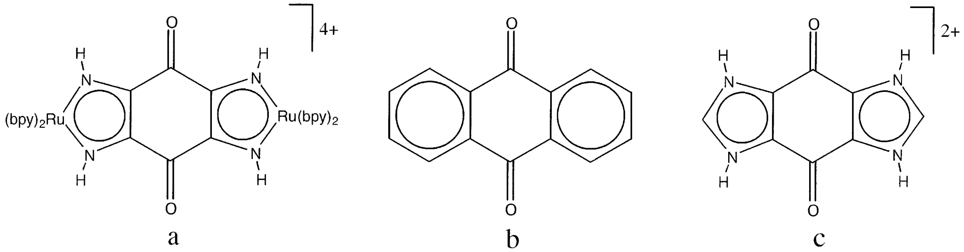

Fig. 12. Structural insights that arise when viewing transition metal complexes such as the tetraiminodiketocyclohexane bridged complex, **a**, from a metalloaromatic perspective. The complex has similar structural features as anthraquinone, **b**, and (*p*-benzoquinono)diimidazolium ion, **c**.

10. The metalloaromaticity controversy

Apart from the use of the term ‘aromaticity’ itself, the controversy surrounding metalloaromaticity mainly stems from work on the α,β-unsaturated complexes, **2**. As it has been stated by Black et al., “aromaticity and quasi-aromaticity have been invoked for these (EAS) reactions, but are in general unnecessary [130].” Indeed, the ligand itself has the propensity to undergo EAS reactions when forced into a planar configuration, as is seen in the dihydrodiazepinium salts [41]. These highly stable salts undergo the same type of EAS reactions as metal acetylacetonato complexes, yet there is no cyclic π-conjugation, and therefore, no possibility of resonance energy stabilization. Furthermore, the NMR spectra of numerous acetylacetonato complexes do not give compelling evidence that a metallacyclic ring current is, in fact, generated by coordination [95,131]. In most cases, the chemical shift of ligand’s central proton varies by only 0.1 ppm whether or not the metals are able to π-bond. The ligands themselves have some aromatic qualities, and as mentioned before, already have a π-sextet of electrons.

The metal-free α,β-unsaturated ligands’ aromatic quality appears to have a different origin than that of aromatic compounds [132]. Using ab initio calculations, Ichikawa partitioned the total energy of a series of cyclic-polyenes into their electronic potential energy and electronic kinetic energy components. A correlation between the kinetic energy per electron and the resonance stabilization energy was found, and it was concluded that aromatic stability is caused by the reduction of the electronic kinetic energy at each atom by allowing delocalization between atoms [131]. When aromatic compounds such as benzene and naphthalene are protonated to break the cyclic conjugation, the rise in total energy is dominated by an increase in the kinetic energy of the electrons whereas, when the α,β-unsaturated ligands, **2**, are protonated, the total energy rises mainly because the *potential energy* of the electrons rise. Thus, the origins of the stabilizations are fundamentally different.

The a_2 and b_2 bonding modes also introduce a complication for these ligands as it becomes difficult to delineate which mode is participating in the π-bonding. Thus, there are very few metals that the ligand does not chelate, and even if the stabilization resulting from each bonding mode is not great, taken together, it may become appreciable.

11. Final remarks

Recent works of Robinson on cyclogallene anions [133], and Sekiguchi et al. on cyclogermanium cations [134] have demonstrated the ultimate extension of the isolobal fragment replacements. Every carbon atom of Breslow’s triphenylcyclopropenium cation [135] has been replaced by a metal fragment. Both of these three-membered cyclic compounds have two π-electrons, and appear to have aromatic properties. The metal–metal distances are unusually short but of equal length, and the compounds are colored, most likely due to a $\pi \rightarrow \pi^*$ transition. The NICS value for the gallium compound is also very negative (-15 ppm) [136] and theoretical calculations show extensive π-bonding in support of the existence of aromaticity.

A number of questions remain regarding metalloaromaticity in transition metal chelates. These mainly arise from the difference in the symmetry of d-orbitals versus p-orbitals. For example, what is the correct description of the aromaticity, ring currents, and delocalization in planar complexes like bis(acetylacetonato)nickel (II) or trischelates such as tris(α,α′-diimine)iron(II)? Is there delocalization of electrons amongst the chelate rings, or should each metallacycle be regarded as a discrete aromatic ring? If there is delocalization between rings, how do the ring currents circulate throughout the complex?

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